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Characteristics of speciation of heavy metals in municipal sewage sludge of Guangzhou as fertilizer

Liang Hei *, Pingwei Jin, Xiaoping Zhu, Weicong Ye, Yanting Yang

Key Laboratory of the Pearl River Estuarine Dynamics and Associated Process Regulation, Ministry of Water Resources, Pearl River Hydraulic Research Institute, Pearl River Water Resource Commission, Guangzhou 510611, China

Abstract

Application of municipal sewage sludge to agricultural land especially in shallow soils, demands to validate the maximum amount of heavy metal, monitoring its effects on soil and on plants. The use of sewage sludge as a fertilizer and soil amendment has resulted in high concentrations of heavy metals in the soil and food limiting its use. Controlling the pollution of heavy metals is the key factor to realize the safe utilization of sewage sludge. In the present study, the heavy metal stabilizers were added to sludge contained in used plastic containers, through artificially watering or naturally rain falling, the nutrient components flowed out with leaching water and fertilized plants but the heavy metals retained in the sludge within container. The potential toxic risks from heavy metals of sludge depend on their chemical speciation. The contents of heavy metals in different treatments were analyzed and their speciation was determined. The pot experiments with plants *(Zea mays and Laetuca satiuali)* showed that the positive effects of the mixture of the sludge and K_2SO_4 on plant production and reduction of heavy metal contents in plants were significant. The BCR sequential extraction procedure was applied for measurement of heavy metals in the experimental sludge. The results showed that the concentrations of Zn were predominant in acid exchangeable and reducible fractions, and Cu was principally distributed in oxidizable fractions. Metals-bound sludge could be collected easily after treatment to prevent the secondary pollution, provided the heavy metals were fixed within the container and reduced obviously the leaching of heavy metals to soil.

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1. Introduction

In the past decades, the demand for higher food production and the increase in exploitation of marginal land

* Corresponding author. Tel.: +020-8511-6685; fax: +020-8511-6685.
E-mail address: hidige@sina.com.cn

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for agricultural food production lead to strong dependence on inorganic fertilizer in the agricultural system in China. However, the uncontrolled use of inorganic fertilizer especially N fertilizer have caused a serious deterioration of the soil and water resources in China, especially for the economic blooming South China. The use of organic fertilizer to partly replace the current practice in uncontrolled use of inorganic fertilizer is the only means to remedy the poor soil quality.

On the other hand, tremendous amounts of sewage sludge are generated daily in China which requires careful handling and disposal to reduce its impact on the environment. Land application is the most popular disposal method but it may entail environmental hazards and decrease plant growth[1,2], which is also the main disposal outlet in industrialized countries[3,4]. In agriculture, crop yield decrease following sewage sludge application has been attributed to high concentration of heavy metals[5] and to phytotoxic substances in the sludge[6]. However, sewage sludge contain very high fractions of organic matters, and organic N and P that represent excellent sources of organic ameliorants for degraded soils [7]. Sludge as Guangdong lateritic red soil crop fertilizer could get the highest fertilizer-use efficiency, and avoid the environmental risk caused by direct agricultural sludge.

2. Materials and methods

2.1 Soils and sewage sludge used

The red soil was sampled in Southern China, and air-dried and screened through a 5 mm sieve. Sewage sludge was an undigested and dewatered sewage sludge obtained from Datansha Wastewater Treatment Plant of Guangzhou. The chemical and physical properties of the soil and sewage sludge are presented in Table 1. According to the Chinese National Standards of Sewage Sludge for Agricultural Application, the main contaminated metals are copper and zinc, other toxic metals were not severely exceeded the standards[8].

Table 1. Physical and chemical characteristics of the soil and sludge.

	Soil	Sludge I	Sludge II	Std for agric. Use*	
				pH< 6.5	pH >6.5
Total Zn, mg/kg	98.8	1362.1	1789.6	500	1000
Total Cu, mg/kg	18.4	287.9	236.5	250	500
Total N, g/kg	1.81	29.7	34.5		
Total P, g/kg	0.64	20.8	26.8		
Total K, g/kg	2.70	18.2	18.9		
Organic matter, g/kg	28.76	313.12	336.0		
Water content, g/kg	25.0	828.6	812.0		
pH (1:2.5 soil:H_2O)	5.65	7.10	7.03		
Germination index, %	60.1	70.0	65.6		
E.coli, MPN/g	/	5.2×10^5	4.9×10^5		

*Chinese national standard (GB4284-1984) of sewage sludge for agriculture use on the soils with soil pH< 6.5 and pH > 6.5 respectively. Sludge I is for Experiment I (the experiment of corn), Sludge II is for Experiment II (the experiment of leaf-used lettuce).

2.2 Experimental design

The following diagram was designed: 15kg of soil was contained in each pot, and fresh sludge (weighted by dry sludge: dry soil=1:100) was filled into each plastic bottle (made by scrap plastic bottle). 10 small holes with diameter of 1 cm were made at 1 cm from the bottom of each bottle. No nutrients were added to the soil in this study. The experiments were undertaken out-door and in 4 replicates.

8 types of treatments were considered as follows: 4 pots, each contained only soils (control 1); 4 pots, each contained soils mixed with sludge (control 2); 4 pots, each contained soils and plastic bottle with fresh sludge;

4 pots, each contained soils and plastic bottle with fresh sludge (mixed with fly ash); 4 pots, each contained soils and plastic bottle with fresh sludge (mixed with K_2SO_4); 4 pots, each contained soils and plastic bottle with fresh sludge (mixed with CaO); 4 pots, each contained soils and plastic bottle with fresh sludge (planted with 3 *Sedum alfredii Hance*); 4 plastic bottles, each contained only fresh sludge (sundried).

2.3 Soil analysis and sludge analysis

At the end of experiments the soil and sludge samples were air-dried, ground to 1 mm and 0.125 mm sieves to analyze their properties. The water, pH, organic matter, N, P, and K were determined according to conventional methods for the samples[9]. Total Cu, Zn and Cd contents in sludge and soil were determined by attacking about 0.3000-0.5000 g of dried samples with $HCl\text{-}HNO_3\text{-}HF\text{-}HClO_4$ mixture followed by elemental analysis (GB/T 17138-1997). The cress (*Lepidium sativum L.*) seed germination index was monitored according to the following formula [10].

$$\text{Germination Index (\%)} = \frac{\text{(Seed germination (\%) X root length) of treatment}}{\text{(Seed germination (\%) X root length) of control}} \text{X100\%}$$

The sequential extraction scheme proposed by Ure et al. (1993) [11] was adopted to partition the heavy metal into four fractions: water-soluble and exchangeable, Fe-Mn oxides, organic matter and sulphides and residual. Each fraction was defined as table 2.

Table 2. Sequential extraction procedure for the speciation of heavy metal.

Fraction phase	Extraction agent	Operation condition
I Water-soluble and exchangeable	0.11mol/L CH_3COOH	Shaken 16 h, centrifuged at 3000 xg, 10 min, and filtered through Whatman No.40 paper.
II Fe-Mn oxides	0.1 mol/L NH_2OH. HCL (pH 2.0 adjusted with HNO_3)	Shaken 16 h, centrifuged at 3000 xg 10 min, and filtered through Whatman No.40 paper.
III Organic matter and sulphides taken	30％H_2O_2	Added 10 ml 30％ H_2O_2 for 1 h in the cold and to dryness on a water bath heated to 85℃; added a second 10 ml 30% H_2O_2, and repeated operation given above.
	1mol/L NH_4OAc (pH 5.0 adjusted with HOAc)	Added NH_4OAc 25 ml, shaken 16 h, centrifuged at 3000xg 10 min, and filtered through Whatman No.40 paper.
IV Residual	Total-(I+II+III)	

2.4 Plant Culture and analysis

Two kinds of plant were planted in this study: one is corn (*Zea Mays*), the other is the other is leaf-used lettuce (*Laetuca Satiuali*). Seeds of corn (Yunshi 5, obtained from Yunnan Province) were sown directly in the pots. At the appearance of the first two leaves, the seedlings were thinned at random leaving three plants per pot. The plant materials of *Sedum alfredii Hance* were obtained from an old Pb/Zn mining area in Zhejiang Province, China. Healthy stems were chosen and grown in the basic nutrient soils.

At harvest, different plant organs were separated, and successively washed with tap water and deionised water. Corn was separated into roots, stems, leaves and seeds; Edible tissues of leaf-used lettuces were choosen. Then the samples were first dried at 105℃ for 30min and finally dried at 70℃. Fresh weight (FW) and dry weight (DW) of samples were recorded. The dried plant materials were ground with stainless steel mill and passed through 0.25mm sieve for elemental analysis. Plant samples of 0.500 g were dry ashed at 550℃ and dissolved in 1:1 (v:v) HCl, then diluted to 25 ml with deionised water, filtered. Heavy metal concentrations of the solution were determined by atomic absorption spectrometer (AAS).

2.5 Statistical data and analysis

Analysis of variance (ANOVA) was performed on all the data sets. Duncan's multiple range test was used for comparison between treatments means. Means and standard errors were presented for all data. The statistical analysis was performed using a statistical package (SAS 8.1).

3. Results and discussion

3.1 Production of plants and heavy metal in plants

Table. 3 gives the total dry-biomass of plants in the pot experiments, and the yield results of the two kinds of plants (*Zea Mays and Laetuca Satiuali*) treatments are basically the same. The yield of plants in pot experiments showed that the two control (no application of sludge treatment and soil mixed with sludge), mixed treatment is clearly more conducive to the increase in plants production. Sludge and fly ash mixed treatment on plants yield for the most significant, compared with the two control was significantly higher than non-sludge treatment, and sludge mixed with soil compared to the control, no significant differences. The three treatments of sludge mixed lime, sludge planted with *Sedum alfredii Hance* and sludge mixed with fly ash had little difference. The treatments of single sludge and the sludge mixed with K_2SO_4 were between the two controls treatments, and there was no significant difference.

Table 3. Dry-biomass of plants. (g/pot DW).

Treatments	Different organs of corn Roots	Stems	Leaves	Seeds	Leaf-used lettuce Edible tissues
Soil	5.01±0.59 c	30.65±5.48 ab	21.98±1.34 b	——	9.57±0.14 b
Soil+Sludge	9.63±0.36 ab	24.79±2.24 b	40.71±2.37 a	39.12±4.28 a	30.98±5.34 a
Sludge	8.42±0.63 ab	34.33±2.41 ab	34.66±2.56 a	12.34±2.93 b	13.03±3.17 b
Fly ash	10.93±0.87 a	38.44±5.84 ab	38.78±2.56 a	40.51±5.93 a	14.95±1.74 b
K_2SO_4	6.59±1.34 bc	34.37±4.89 ab	35.47±1.99 a	22.56±1.86 b	21.52±1.70 a
CaO	10.79±0.99 a	47.14±6.31 a	38.10±3.65 a	10.46±1.21 b	11.38±2.03 b
Sedum	10.27±1.50 a	39.15±5.55 ab	35.54±2.77 a	20.13±3.32 b	9.34±1.75 b

All data values represent the means ± standard error (n=4); Within a column values followed by the same lowercase letter are not significantly different from one another at p=0.05.

Table 4 lists the heavy metal concentrations of Zn and Cu in the various organs of *Zea Mays and Laetuca Satiuali*. There were significant differences ($p<0.05$) among the treatments. Of all the heavy metals examined in the sludge treatment , the concentration of Zn or Cu was the highest, which was due to the smallest biomass in plants in the process (table 3), and in which the body produces heavy metal concentrated effect, but made the most of its heavy metal concentrations performance. The highest Zn in the edible tissues of leaf-used lettuce was in the treatment of soil mixed with sludge, a significant difference compared with other treatments. Since no sludge treatment used red soil, where nutrient deficiency, insufficient to provide the necessary nutrients for plant growth, resulting in growing corn was not good, no seed. For different plant species, the concentrations of Zn and Cu in the plants were different, such as Zn concentrations, maximum was 394.5 mg/kg in the leaves of soil mixed sludge treatment, and minimum was 24.1mg/kg in the corn seeds of sludge treatment. Therefore, leafy vegetables are more easily than seed plants enrichment of heavy metals. In China, serious contamination of heavy metals in vegetables and farmlands poses a threat to human health. Leafy vegetable is one of the most widely planted, and largest consumed, but also the most vulnerable to heavy metal contamination category of vegetables with many varieties. Therefore, study on the accumulation characteristics of heavy metals in leafy vegetables and the soil critical values for food safety is desirable, which has an important guiding role in improving the quality and safety of agricultural products.

Table 4. The concentrations of Zn and Cu in plants (mg/kg).

Treatments	Different organs of corn				Leaf-used lettuce
	Roots	Stems	Leaves	Seeds	Edible tissues
Zn					
Soil	125.95±14.58 a	146.77±9.52 bc	27.33±4.09 b	——	209.5±9.20 e
Soil+Sludge	114.97±16.38 ab	311.69±32.63 a	64.22±5.62 a	25.97±1.34 ab	394.5±14.3 a
Sludge	76.12±8.04 c	111.01±10.29 c	26.30±1.42 b	24.10±1.77 b	286.6±11.8 cd
Fly ash	86.45±5.56 bc	137.77±11.18 bc	34.43±4.05 b	26.99±1.82 ab	328.0±4.90 bc
K_2SO_4	100.71±5.07 abc	127.39±15.63 bc	29.03±2.81 b	26.73±3.77 ab	270.2±13.8 d
CaO	88.28±4.76 bc	175.10±18.11 b	28.51±2.84 b	31.42±2.66 a	303.6±9.0 bcd
Sedum	111.75±10.92 ab	147.70±9.11 bc	24.85±1.80 b	25.06±1.68 ab	339.3±31.3 b
Cu					
Soil	31.08±3.52 a	2.31±0.05 abc	5.61±0.05 ab	——	9.40±0.40 d
Soil+Sludge	13.06±1.35 c	3.16±0.19 a	5.63±0.55 ab	2.63±0.20 a	10.1±0.50 d
Sludge	12.95±1.53 c	1.96±0.18 bc	4.09±0.26 bc	2.29±0.04 a	10.7±0.60 ab
Fly ash	16.47±1.21 bc	1.86±0.19 c	3.91±0.41 c	2.06±0.16 a	12.8±0.22 c
K_2SO_4	20.34±1.84 b	2.01±0.20 bc	5.69±0.97 ab	2.29±0.21 a	14.3±0.06 a
CaO	18.76±1.98bc	2.61±0.26 abc	4.61±0.47 abc	2.48±0.13 a	12.0±0.72 bc
Sedum	15.72±1.77 bc	2.79±0.48 ab	5.85±0.50 a	2.05±0.64 a	12.2±0.71 bc

All data values represent the means ± standard error (n=4); within a column values followed by the same lowercase letter are not significantly different from one another at p=0.05.

3.2 Heavy metal fractions in sewage sludge

Many studies showed that the toxicity of heavy metals was not only relating to the total contents but also dependent on the chemical fraction of heavy metals. The environmental behaviours and bio-toxicity of heavy metals vary in different chemical fractions of heavy metals. Bioavailability of heavy metals refers to the degree to which these metals are adsorbed or accumulated in organisms. Total metal concentration is not a very useful predictor of bioavailability or soluble concentration of the metal [12.13]. The determination of total heavy metal content of sludge was not sufficient to evaluate the possible mobility and consequently, the bioavailability of toxic metals to living organisms [14]. The environmental effect s of heavy metals vary in different chemical fractions: exchangeable metals were easy to transport and transform and could be absorbed by plants ;Carbonate bound metals were susceptible to pH, it could be remobilized and released in the acidic environment in the rhizosphere and be taken up by plants[15,16], and therefore , could harm human health through the soil-plant -human body chain; Fe-Mn oxides bound metals were not easy to release under normal conditions for the relatively strong ionic bonding; The organic fraction released in the oxidizable step is not considered very mobile or available since it is thought to be associated with stable high molecular weight humic substances that release small amounts of metals in a slow fashion[17]; The residual fraction, consisting of metals retained within the crystal lattice of minerals and well crystallized oxides is considered to be immobile[17,18]. So it is necessary to analyse the chemical fractions of each metal, the distribution of the metals determined by sequential extraction is shown in Fig.1- Fig.4.

As shown in Fig.1 (Experiment I), the predominant form of Zn was reducible fraction, which accounted for about 40%. The next was exchangeable fraction, which accounted for about 28%. The proportions of oxides and residual were lower, which was about 22% and 10% respectively. After planting *Laetuca Satiuali*, the distribution characteristics of Zn fractions had changed, in the sludge of Experiment I were as follow: residual < oxides < exchangeable < reducible, but in the sludge of Experiment II were as follow: oxides < residual < reducible < exchangeable.

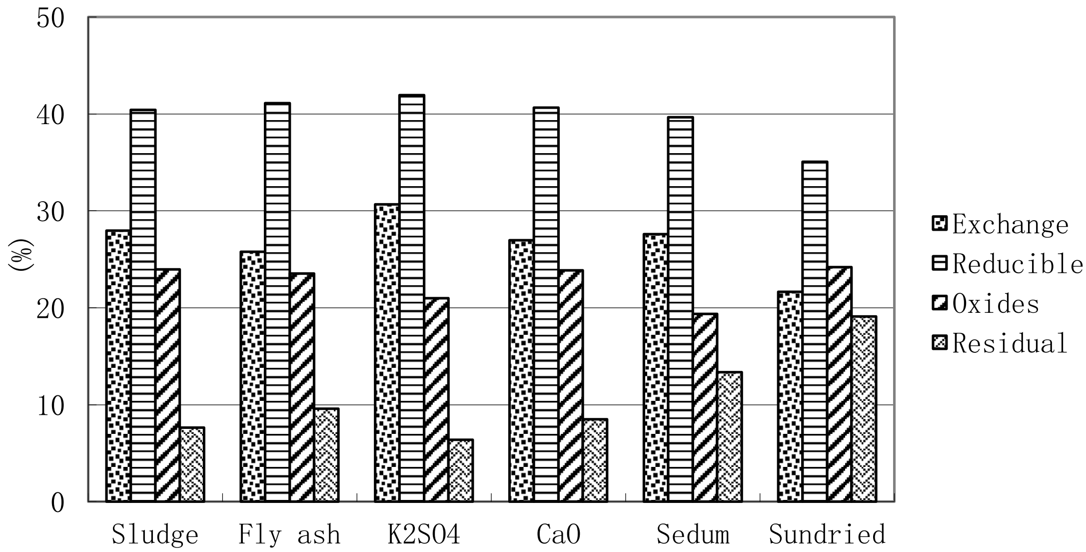

Fig.1 Zn distribution in sludge of experiment I

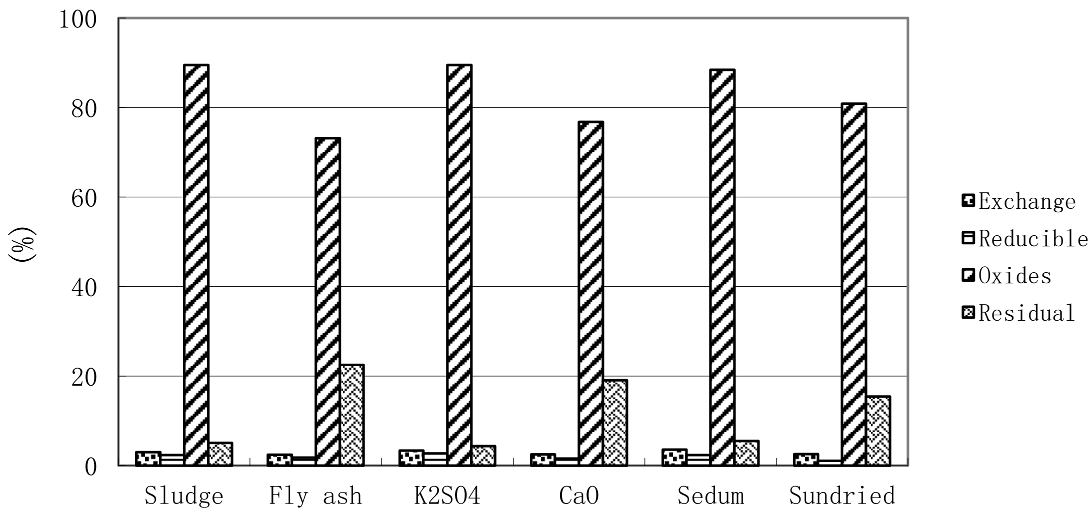

Fig.2 Cu distribution in sludge of experiment I

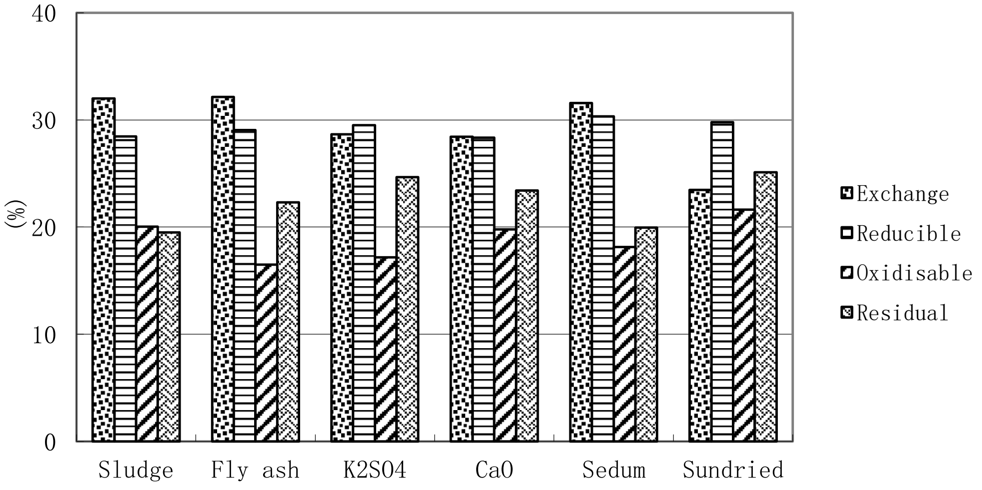

Fig.3 Zn distribution in sludge of experiment II

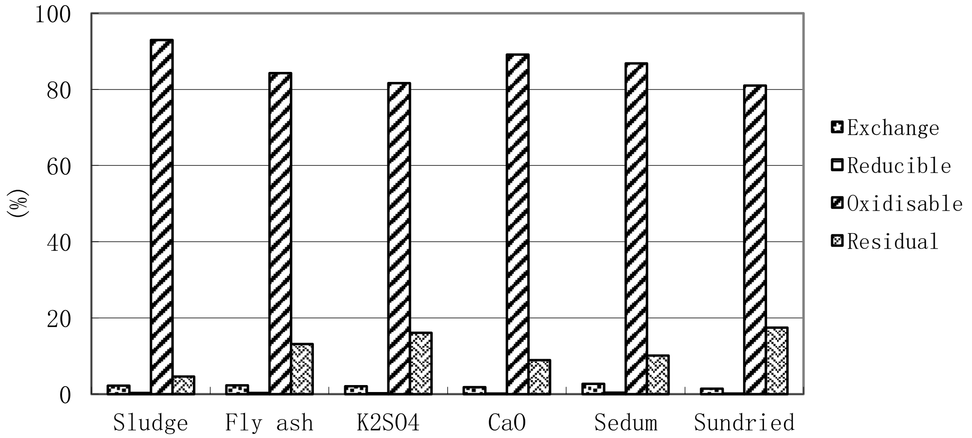

Fig.4 Cu distribution in sludge of experiment II

As shown in Fig.2 (Experiment I), the predominant form of Cu was oxides fraction, which accounted for about 83%. The next was residual fraction, which accounted for about 12%. In Fig.2 and Fig.4, the content of reducible fraction was too low to be measured. The proportions of exchangeable and reducible were lower, which was about 3% and 2% respectively. After planting *Laetuca Satiuali*, the distribution characteristics of Cu fractions hadn't changed, in the sludge of Experiment I and II were the same as follow: reducible < exchangeable < residual < oxides.

From the above, it could be concluded that the concentrations of Zn were predominant in acid exchangeable and reducible fractions, and Cu was principally distributed in oxides fractions. Metals-bound sludge could be collected easily after treatment to prevent the secondary pollution, provided the heavy metals were fixed within the container and reduced obviously the leaching of heavy metals to soil.

3.3 Sludge fertilization and stabilization

Although there was a significant decrease in P and K compared to the fresh sludge, the amendments were still comparable to those for cow dung [2], which has also been recommended for use as a fertilizer [19]. The chemical compositions of the sludge after the twice cropping reinforced the potential fertility of this medium showing that the sludge should therefore be capable of supporting subsequent cropping.

Table 5. Concentrations of NPK in sludge after experiment I and II (g/kg).

Treatments	N	P	K
Fresh sludge	34.5 a	26.8 a	18.9 a
Sludge	32.1 a	19.0 b	13.8 c
Fly ash	32.3 a	19.3 b	14.0 c
K_2SO_4	33.7 a	20.4 b	15.5 b
CaO	33.2 a	20.1 b	12.9 d
Sedum	31.8 a	18.9 b	13.4 cd
Sundried	33.2 a	24.6 a	17.0 a

Within a column values followed by the same lowercase letter are not significantly different from one another at p=0.05.

4. Conclusion

The sewage sludge mixed with fly ash, lime and K_2SO_4 was contained in used plastic containers. Through naturally rain falling or artificially watering, the fertilizer components flowed out and fertilized soils while the heavy metals were fixed within the container, which reduced obviously the soil contamination by heavy metals.

The cultures of *Zea mays* and *Laetuca satiuali* showed the positive effect of the mixture of sludge and K_2SO_4 on plant production and reduction of heavy metal content in plants. The plastic containers make sewage sludge useful as organic fertilizer resource and decrease the contamination of soils and plants by the heavy metals in the sludge. Besides, this method permits the plastic waste recycled and reutilized with a low cost.

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